ANNOTATION

the dissertation work of Omarov Bekzhan Temirkhanovich on the topic "Development of innovative technology for the production of humate-containing complex mineral fertilizers" submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D072000-"Chemical technology of inorganic substances"

The relevance of the topic.

The Republic of Kazakhstan is actively engaged in agriculture, and improving the quality of agricultural products has become a pressing issue today. Recycling industrial waste is also among the urgent and unresolved problems facing the country. Researching ways to produce humate-containing mineral fertilizers using natural raw materials and industrial waste is one of the key tasks.

One of the main elements of soil fertility is the presence of N, P, K, humic substances, and microelements. The only solution to this issue is the establishment of humate-containing fertilizer production.

Coal mines generate millions of tons of low-calorie coal waste, unsuitable for combustion, which forms in the oxidized surface layers of deposits and tends to self-ignite.

A review of literature and patents has shown that using natural raw materials and industrial waste for the production of humate-containing fertilizers not only reduces environmental pollution but also makes it possible to produce inexpensive fertilizers.

The raw materials used for fertilizer production include phosphorous production waste, such as tertiary return fines, cyclone dust, and electrofilter dust generated after the AKM-312 agglomeration machine. Their composition includes P_2O_5 (total) ranging from 19.8% to 22.86%, as well as oxides of Ca, Mg, K, Na, S, and F, along with microelements that promote plant growth and development.

The proposed technology for producing complex organomineral fertilizers from brown coal humates is simple and does not require significant financial investment.

Thus, the development and implementation of innovative technologies for the production of such fertilizers are important and relevant tasks.

The purpose of the study: to develop an innovative technology for the production of humate-containing complex mineral fertilizers.

Research objectives:

- determining the quality of raw materials (brown coal, phosphate dust, vermiculite, etc.) and studying their suitability for the production of humate-containing organomineral fertilizers using physicochemical methods;
- improving the process of obtaining humates in a hydrodynamic rotary-pulsation apparatus;
- identifying the technological parameters for obtaining humates from brown coal (temperature, alkali concentration, extraction time);
- developing the technology and technological scheme for producing humates and humate-containing fertilizers using brown coal from the Ekibastuz deposit;

- investigating the impact of humate-containing fertilizers on soil fertility and the productivity of agricultural crops.

The object and methods of research.

The equipment used for extracting humates from brown coal through alkali treatment includes devices for processing tertiary return fines generated during phosphate agglomeration, electrofilter dust, cyclone dust, vermiculite, inner geological layers, ammophos, and sulfur-based raw materials. Using modern equipment, the production of humate-containing complex organomineral fertilizers was carried out with the following instruments: an electronic microscope JEOL JSM6490 LV, a TGA/DSC1 METTLER TOLEDO calorimetric device for thermographic analysis and differential scanning, a SPECORD 75 IR spectrophotometer, and a Q-derivatograph STARS SK for differential structural analysis.

The research methods included analytical, physicochemical, thermodynamic, and kinetic techniques, along with statistical and mathematical methods for processing and analyzing experimental data. Traditional methods and approaches were also employed for conducting field tests of fertilizers on various agricultural crops.

The main provisions submitted for protection:

- the yield of humates is 65% as a result of processing brown coal, phosphorite dust, vermiculite, and other raw materials;
- optimal technological parameters for obtaining humates from brown coal: temperature of 70°C, sodium hydroxide solution concentration of 15%, extraction time of 10 minutes, with a humate yield of 65%;
- the use of a hydrodynamic rotor-pulsation apparatus increases the efficiency of the humate production process. This technology reduces production time and improves product quality;
- the application of humate-containing fertilizers in agriculture increases the yield of grain and vegetable crops by 15%-50%. Additionally, they improve the structural, chemical, and biological properties of the soil;
- recycling industrial waste ensures environmental safety. This approach enhances the economic efficiency of humate-containing fertilizer production technology and addresses environmental issues.

The main results of the study:

1. When producing complex organomineral fertilizers containing humates, the use of hygroscopic vermiculite as a raw material, which is safe for agricultural crops, insoluble, non-degradable, and water-retentive, allows saving up to 10-15% of water during the irrigation of vegetable crops.

2. The thermodynamic and kinetic dependencies of the main reactions occurring during the production of complex organomineral fertilizers containing humates have been determined. Using a hydrodynamic rotary-pulsation apparatus, the transition process from brown coal to humates takes 15-20 seconds.

3. Thermodynamic and kinetic studies of the processes of obtaining humates and purifying brown coal from impurities showed that for six studied reactions, in the temperature range of 298-351 K, enthalpy values are negative and range from

211.0 to 2067 kJ/mol. The reaction of iron oxide decomposition with sulfuric acid is characterized by values ranging from 4949.1 to 5119.5 kJ/mol, indicating the thermodynamic feasibility of this reaction.

4. Experimental studies of the process of obtaining humates from brown coal depending on alkali concentration were processed using the Pavlyuchenko equation. The calculation of the apparent activation energy based on the graphical dependence lnk=f(1/T) showed that its values range from E_{pred} = 66.6–109.3 kJ/mol. This process is characterized by adsorption occurring in the transitional kinetic zone, along with the active influence of diffusion factors.

5. The main technological indicators of the process of obtaining complex fertilizers containing 45% humates, 30-35% phosphorus-based solid residues, 9-11% vermiculite, and 8-12% inner geological layers rich in potassium and microelements generated during coal production have been developed.

6. Field trials of organomineral fertilizers conducted on the croplands of the "Zhantas" farm and the leased lands of the South Kazakhstan University named after M. Auezov in the village of Zhaskesh, Tyulkubas district, allowed identifying the agronomic role of humic substances. It has been established that humic substances improve soil structure, aeration, water retention, and water release capacity, increase the yield of various agricultural crops by 15-50%, prevent soil acidification, and reduce the formation of soil cracks.

The use of humate-containing and moisture-retaining substances allows increasing production efficiency while saving 10-15% of water for irrigation and retaining moisture in the soil.

Substantiation of the novelty and importance of the results obtained:

- the optimal ratio of raw materials was determined during the roasting process of a mixture containing phosphate fines, vermiculite, cyclone dust, and inner geological layers at a temperature of 700-800°C for 10-20 minutes. The release of carbon dioxide and moisture increases the porosity of vermiculite, while carbonates and sulfur compounds decompose from the inner geological layers;

- during the process of adding sulfuric acid to coal, within the temperature range of 298-351 K and under the influence of time, chemical reactions occur between the components, resulting in the formation of oxides such as K_2O, Na_2O, CaO, Al_2O_3, Fe_2O_3 and MgO. Diffusion displacement is observed in this process, facilitating the redistribution of reaction products and their transition to equilibrium. The study results showed that the diffusion displacement level reached 92.3%, while the remaining 7.7% of the process products indicated stabilization. These results demonstrate that the main part of the reaction was completed, the chemical system achieved a stable state, and the process acquired a steady nature;

- experimental and field tests of humate-containing organomineral fertilizers on various vegetable crops revealed that adding vermiculite to the fertilizer improves porosity, resulting in moisture retention in the soil and enabling water savings of up to 10-15% during irrigation periods;

- it was found that processing hydrocarbon suspensions in a hydrodynamic rotary-pulsation apparatus (HRPA) increases the humate yield by 2-3 times, reaching up to 65%.

The theoretical significance of the work lies in carrying out theoretical and experimental studies to identify the optimal technological and technical characteristics of the main and auxiliary equipment, devices and installations.

The practical significance of the work:

- Development of the technology and technological scheme for producing humate-containing organomineral fertilizers, including the determination of optimal technological and technical characteristics of primary and auxiliary equipment, apparatuses, and installations.

- Optimal technological parameters for carrying out the process of obtaining humate-containing organomineral fertilizers.

- Optimal parameters for grinding phosphorus- and humate-containing materials, confirmed by the innovative patent of the Republic of Kazakhstan No. 31226 “Method of grinding phosphorus-containing materials.”

- Production of non-granulating and non-sticking organomineral fertilizers containing humic substances by utilizing technogenic and natural raw material waste from various industrial sectors to improve the ecological condition of industrial regions.

Compliance of the dissertation with the directions of scientific development or state programs. The dissertation work was carried out at the Department of "Technology of Inorganic and Petrochemical Industries" and the scientific-research laboratory "Inorganic Salts, Plant Protection, and Growth Stimulators" of M.Auezov South Kazakhstan University. It aligns with the research work of the Department of Inorganic Chemistry and Technology (ChTIS) as part of the state budget program for 2016-2022 and the state-funded project 2021-2025 GBPNIR 21-03-02: "Development of new promising technologies for the production of inorganic products, environmentally friendly fertilizers, and plant growth stimulators based on mineral raw materials and technogenic waste, as well as improvement of traditional technologies." Additionally, the work was performed under the project AR15473348 "Development of a new technology for producing complex humate-containing mineral fertilizers," funded through the "Young Scientist-2022" grant program.

The personal contribution of the doctoral student to the preparation of each publication consists in the development of the main provisions, with the development of research results, conclusions of dissertations and works, which are set out in 19 printed works, including in international scientific publications included in the Scopus – 3 database, in journals recommended by the KOKSNVO MNVO RK – 3, in the materials of international conferences – 11 articles, 1 innovative patent of the Republic of Kazakhstan was obtained and 1 monograph was published.

The author's contribution to the preparation of each article is presented in the dissertation.

The structure and scope of the dissertation. The dissertation work consists of an introduction, six chapters, a conclusion, a list of references and appendices. The work is presented on 174 pages, 27 tables, 69 figures. The list of references is 108 titles of literature.